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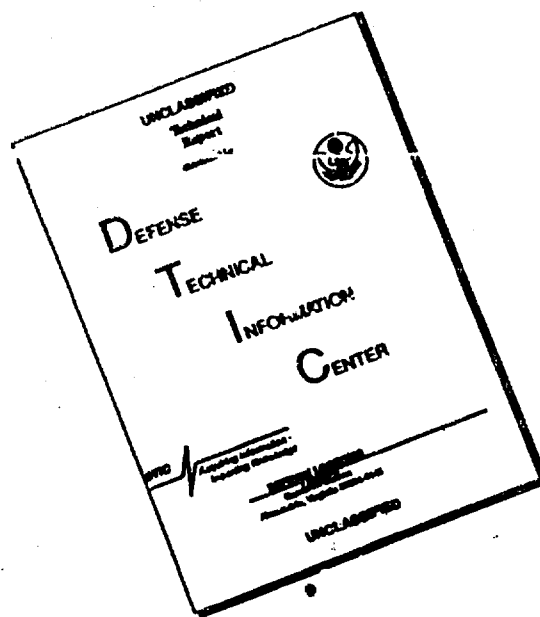
APPLIED POLAROGRAPHY FOR ANALYSIS OF ORDNANCE
MATERIALS

PART 1. DETERMINATION AND MONITORING FOR
1,2-PROPYLENEGLYCOLDINITRATE IN EFFLUENT
WATER BY SINGLE-SWEEP POLAROGRAPHY

NAVAL WEAPONS CENTER

JUNE 1976

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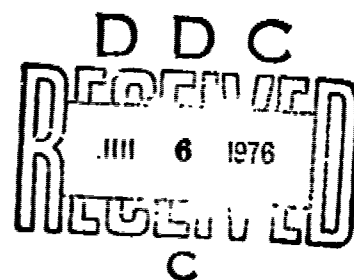
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Applied Polarography for Analysis of Ordnance Materials.

Part 1. Determination and Monitoring of
1,2-Propyleneglycoldinitrate in Effluent
Water by Single-Sweep Polarography

by
Gerald C. Whitnack
Research Department
and
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JUNE 1976

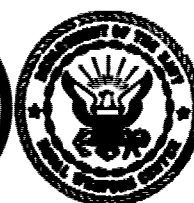
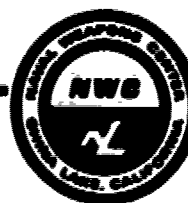


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FOREWORD

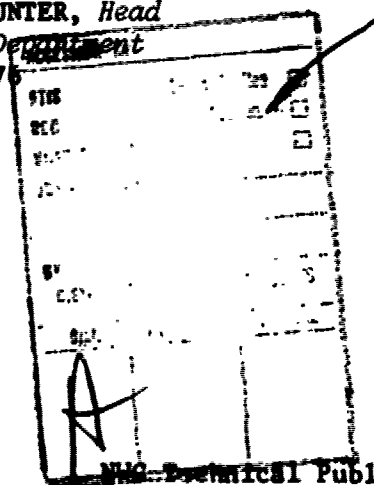
The work described in this report is part of a continuing research project entitled "Applied Polarography for Analysis of Ordnance Materials." This work is supported by the Naval Sea Systems Command, Code 0332, under Task Area Number SF57572301 and represents a final report on Phase I of the work covering the period fiscal years 1975 and 1976.

Phase I of the work is divided into two final reports under the above general title. Part 1 is "Determination and Monitoring of 1,2-Propyleneglycoldinitrate in Effluent Water by Single-Sweep Polarography" and Part 2 is "An Inexpensive Solid-State Field Polarograph With Digital and Analog Output."

This report has been reviewed for technical accuracy by Dr. Arnold T. Nielsen, Robert L. Fowler, and Gordon R. Doyel.

Released by
HUGH W. HUNTER, Head
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10 May 1976

Under authority of
G. L. HOLLINGSWORTH
Technical Director



NWC Technical Publication 5860, Part 1

Published by Technical Information Department
Collation Cover, 11 leaves
First printing 175 unnumbered copies

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWC TP 5860, Part 1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) APPLIED POLAROGRAPHY FOR ANALYSIS OF ORDNANCE MATERIALS. PART 1. DETERMINATION AND MONITORING FOR 1,2-PROPYLENEGLYCOLDINITRATE IN EFFLUENT WATER BY SINGLE-SWEEP POLAROGRAPHY		5. TYPE OF REPORT & PERIOD COVERED Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Gerald C. Whitnack Walter J. Becketl		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task Area SF57572301
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE June 1976
		13. NUMBER OF PAGES 23
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Explosives Analysis Fuels Pollution Propellants Environment Polarography Water		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See back of form.		

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(U) *Applied Polarography for Analysis of Ordnance Materials. Part 1. Determination and Monitoring of 1,2-Propyleneglycoldinitrate in Effluent Water by Single-Sweep Polarography*, by Gerald C. Whitnack and Walter J. Becktel. China Lake, Calif., Naval Weapons Center, June 1976. 20 pp. (NWC TP 5860, Part 1, publication UNCLASSIFIED.)

(U) A new rapid, specific, and unique polarographic method of analysis for 1,2-propyleneglycoldinitrate (PGDN) in effluent water is described. A portable and inexpensive digital polarograph and monitoring system, built at NWC, are presented for the field analysis of PGDN in an effluent water obtained from a Navy carbon column cleanup process to remove the explosive from *Otto Fuel* wastewater. Data obtained by the NWC-developed method of analysis and field equipment compare favorably with data obtained by a vapor-phase chromatographic method on the same samples of effluent water. Part 2 of this report describes in detail the digital polarograph, circuitry, and operational characteristics of the complete polarographic monitoring system.

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NWC TP 5860, Part 1

CONTENTS

Introduction	3
Apparatus and Materials	4
Field Polarograph	8
Clock	10
Sync Control	10
Sweep Generator	10
X-Amplifier	10
Start Potential	10
Power Amplifier	12
Cell Amplifier	12
Summing Amplifier	12
Low Pass Filter	12
Current Compensation	12
Y-Amplifier	12
Analog-to-Digital Converter	12
Experimental	13
Polarographic Analysis for PGDN (With Field Polarographs and A-1660 <i>Polarotrace</i>)	13
Laboratory and Field Samples (Procedure)	13
Digital Polarograph and Monitoring System	15
Results and Discussion	15
Conclusions and Recommendations	18

NWC TP 5860, Part 1

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of personnel at the Naval Torpedo Station, Keyport, Washington, for furnishing the effluent water, and the Naval Ordnance Station, Indian Head, Maryland, for supplying the pure PGDN used in this study.

We appreciate the support of this work by the Naval Sea Systems Command.

INTRODUCTION

The manufacture, storage, and disposal of ammunition, propellants, fuels, and other ordnance material have resulted in the release of many toxic organic and inorganic substances to the environment. At present, the Navy cannot rely on standard methods of analysis for many of its ordnance compounds of concern in pollution control, as either no method exists or the reliability of a method has not been established for environmental samples at the part-per-billion level needed in this work.

The technical objective of this research program is to apply modern polarography and related electrochemical techniques to the analysis of ordnance-related materials where reliable analytical methods are lacking. The work initially has been directed toward the analysis of explosives¹⁻³

¹ Naval Ordnance Laboratory. *ULTRAMICRO Analysis of Explosives in Seawater*, by J. C. Hoffsommer and J. M. Rosen. White Oak, Md., NOL, August 1971. 13 pp. (NOLTR 71-151, publication UNCLASSIFIED.)

² D. J. Glover and J. C. Hoffsommer. "Thin-Layer Chromatographic Analysis of HMX in Water," *Bulletin of Environmental Contamination and Toxicology*, Vol. 10, No. 5 (1973), pp. 302-04.

³ J. C. Hoffsommer. "Quantitative Analysis of Nitro Compounds in the Micro- to Picogram Range by a Combination of Thin-Layer and Vapor Phase Chromatography with the Nickel-63 Electron Capture Detector," *J. Chromatogr.*, Vol. 51 (1970), pp. 243-51.

⁴ G. C. Whitnack. "Determination of Trinitrotoluene in Warhead Exudates by Linear Sweep Polarography," *Anal. Chem.*, Vol. 35 (1963), pp. 970-73.

⁵ Picatinny Arsenal. *Applicability of Raman Spectroscopy to Continuous Monitoring of Pollutants from Army Ammunition Plants. I. Nitroglycerin in Water and II. Tetranitromethane in Air*, by C. S. Freer. Dover, N.J., July and March 1974. (Tech. Rept. 4667 and 4668, publications UNCLASSIFIED.)

⁶ J. S. Hetman. "Application of the Cathode-Ray Polarograph to the Analysis of Explosives," *Advance Polarogr., Proc. Int. Congr.*, 2nd, Cambridge, Vol. 2 (1960), pp. 640-46.

⁷ J. S. Hetman. "Simultaneous Polarographic Determination of Pentaerythritoltetranitrate and Cyclotrimethylenetrinitramine," *Anal. Chem.*, Vol. 32 (1960), pp. 1699-701.

⁸ J. S. Hetman. "Polarography of Explosives," *Z. Anal. Chem.*, Vol. 264 (1973), pp. 159-64.

⁹ G. C. Whitnack. "Single-Sweep Polarographic Techniques Useful in Micropollution Studies of Ground and Surface Waters," *Anal. Chem.*, Vol. 47 (1975), pp. 618-21.

such as 1,2-propyleneglycoldinitrate (PGDN), 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), nitroguanidine, and 2,4,6-trinitrotoluene (TNT) that are connected with Navy-ordnance related facilities. The techniques studied emphasize analysis directly at the part-per-billion level in natural, waste, and effluent water without the necessity for a prior separation or concentration of the explosive from the water, and finally a procedure that can be automated and used in the field on a continuous basis.

It is the purpose of this report to present and discuss a specific, rapid, and reliable single-sweep polarographic method of analysis for PGDN in effluent water that is obtained from a carbon adsorption process used to remove this explosive from a wastewater containing large amounts of a torpedo fuel known as *Otto Fuel*. The analytical procedure and monitoring system was developed in this laboratory and is currently awaiting an on-line test at the Naval Torpedo Station, Keyport, Washington, with the carbon adsorption process being tested there.

A field polarograph has been built recently in this laboratory and with laboratory tests both an analog and a digital unit give data that compare favorably with data obtained by a vapor phase chromatographic procedure^{2,3} currently being used at Keyport to determine PGDN in effluent water. The portable polarographs are inexpensive, solid-state, weigh approximately 13.2 kg (6 lb) each, can be battery operated, and will produce both digital and analog data in seconds during individual or continuous analysis. The instruments (prototype models) are ready for on-site testing in connection with the analysis of PGDN or other compounds of interest to the Navy. A brief description of the circuitry and operation of the field polarographs, with discussion of the entire polarographic monitoring system and analytical procedure for PGDN in effluent water, is presented in Part 1 of this report. Part 2, "An Inexpensive Solid-State Field Polarograph With Digital and Analog Output," describes in detail the circuitry, operational characteristics, and performance of the field polarographs.

Further work is being carried out on "Applied Polarography for Analysis of Ordnance Materials" and phases of this work will be reported as the work is completed.

APPARATUS AND MATERIALS

A single-sweep polarograph with a dropping mercury electrode (DME), known as the A-1660 Davis differential cathode-ray *Polarotrace* and manufactured by Southern Analytical Instruments Company, England, was used to establish the optimum conditions in the laboratory for the analysis of PGDN in the effluent water obtained from the carbon adsorption apparatus used to remove this explosive from *Otto Fuel* wastewater. A Moseley 2D X-Y recorder was used to record the data obtained with this instrument and also data obtained with the field polarographs described in this report.

The complete digital polarographic monitoring system for field or laboratory use is shown in Figure 1. The digital polarograph (digital and/or X-Y data) is shown at the left with a DME constant temperature stand and small volume cell with a stainless steel cylinder (right) for controlling the solution temperature in the large quartz cell shown in the foreground. The DME is inserted into the effluent water sample contained in the cell which has been previously placed inside the constant temperature device. Three solid (carbon-type) electrodes are shown in this figure (left) as potential replacements for the DME in the field, where use of mercury might be prohibitive. The use of these solid electrodes with the system described is the subject of current research in this laboratory.

Figure 2 shows the analog field polarograph (X-Y or strip chart recorded data) with polarographic cell, constant temperature device, and carrying case. This instrument has several controls on the outside panel to allow greater versatility in establishing the optimum conditions for the analysis of different pollutants in aqueous media. In the digital polarograph the analytical parameters are preset inside the case to perform a certain analysis. This ensures that no external knobs are turned which might alter the output data during field analysis.

The polarographic measurements were made at $25^{\circ}\text{C} \pm 0.10^{\circ}\text{C}$ on 2 ml of water placed in a 5-ml capacity quartz cell for most of the laboratory studies. The field polarographic cell holds larger volumes of water and when used with the field polarographs about 15 ml of effluent water is retained in the cell during a measurement of the concentration of explosive. A small stainless steel constant temperature device was built to keep the temperature of the effluent water in the cell to $30^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ in the field.

The DMEs used in this work had drop times of 7 seconds in distilled water on open circuit and $m = 5$ to 7 mg per drop of mercury. Redistilled mercury was used as an anode and for the DME. The current peak potentials are referred to a mercury pool or to a saturated calomel electrode as reference. Since the electroactive specie concentrations measured in this work are extremely low (10^{-6} to 10^{-8} M), the currents are very small and the value of the internal resistance (iR) correction is therefore negligible. pH Measurements were made with a Beckman expanded-scale pH meter.

The PGDN used in this study was obtained from the Naval Ordnance Station, Indian Head, Maryland, and was especially purified at that Station to a level of 99% or better. The polarograms obtained with this material were found proportional to explosive concentration over a range of 5×10^{-6} to 10^{-9} g/ml. Standard solutions of the explosive were prepared in spectroquality acetone, obtained from Matheson, Coleman and Bell. These solutions were prepared in the 10^{-6} to 10^{-5} -g/ml range and then microaliquots (0.01 to 0.05 ml) were added directly to the water sample in the polarographic cell for analysis.

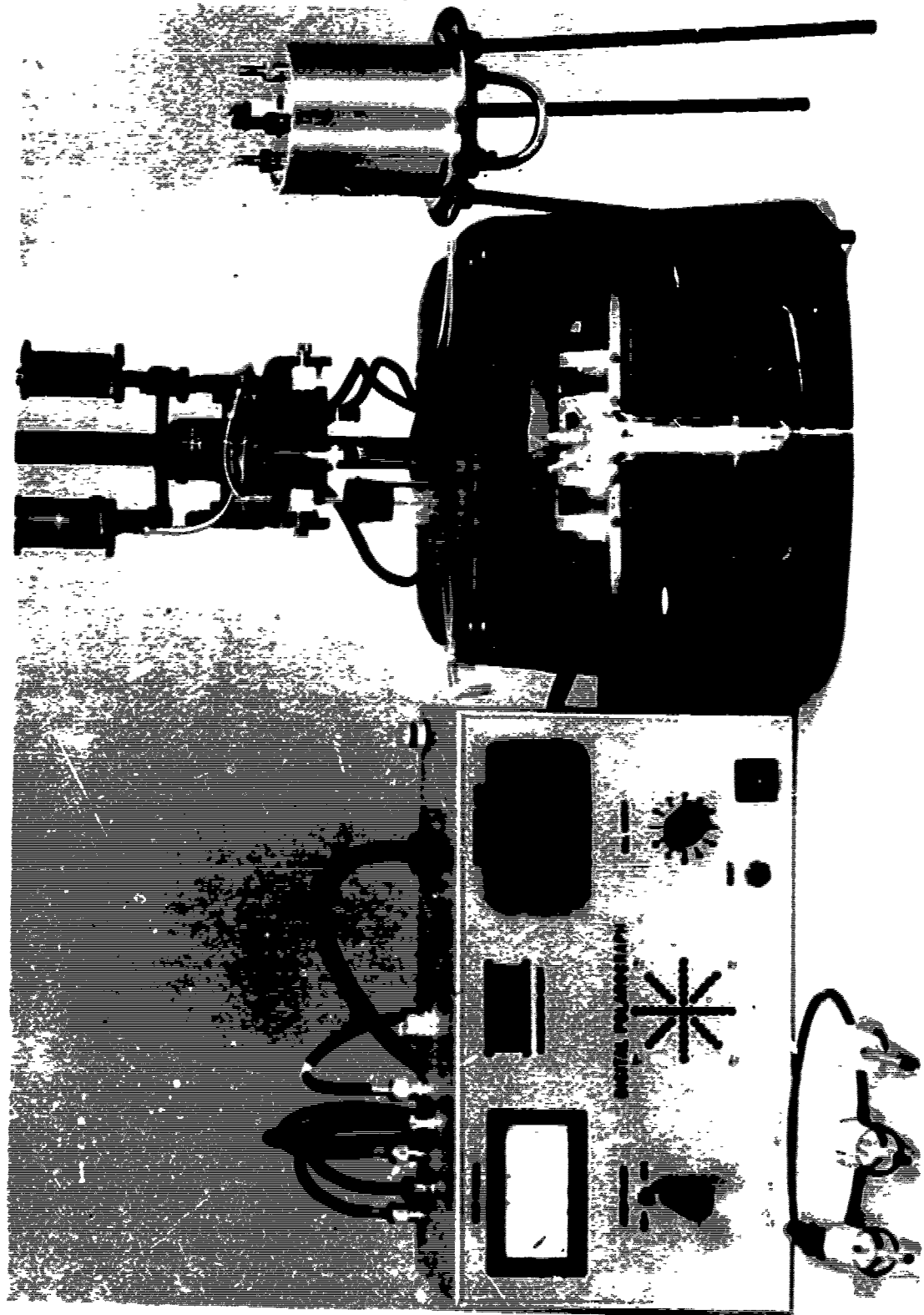
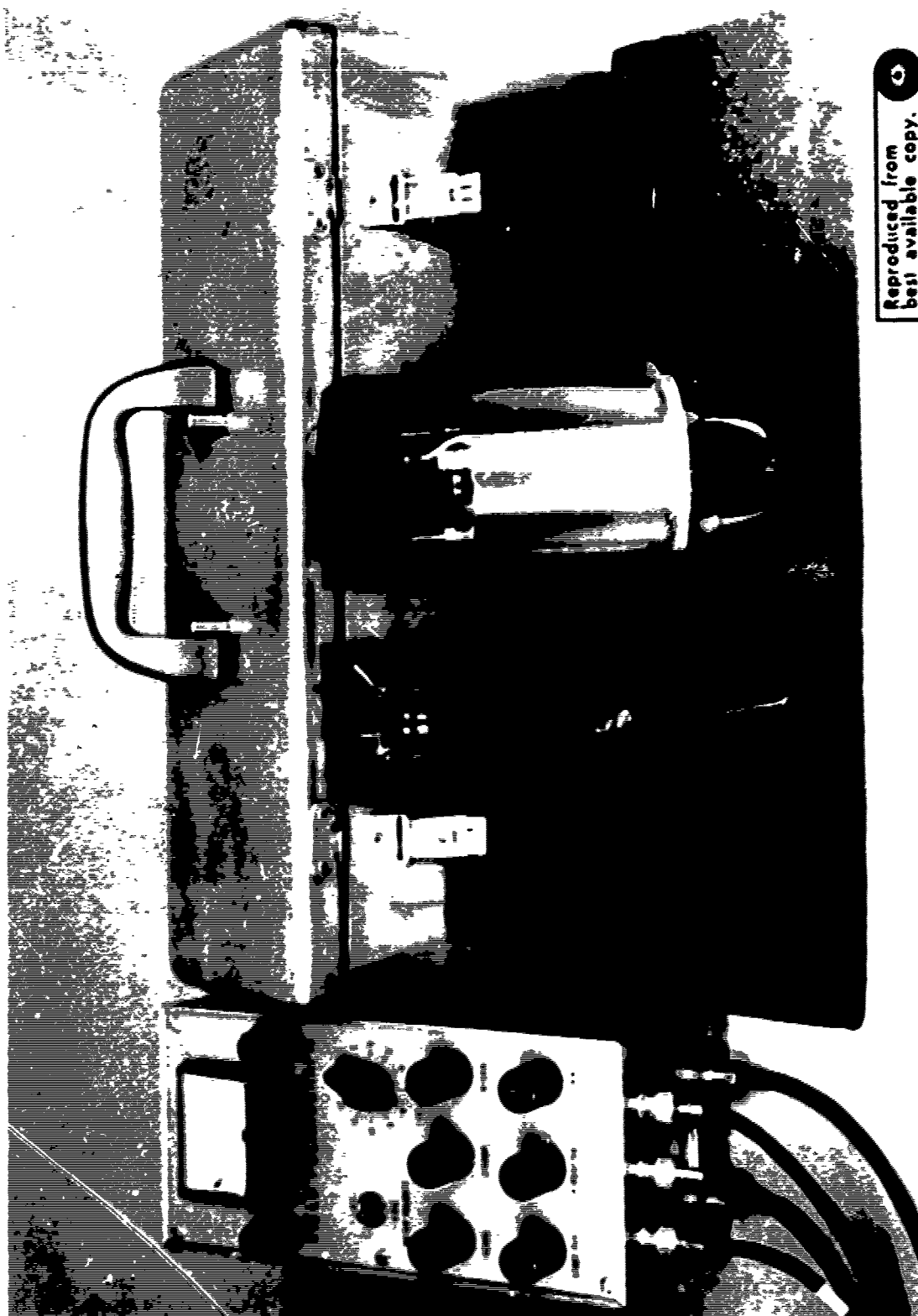


FIGURE 1. Digital Polarograph and Accessories.



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FIGURE 2. Field Polarograph and Accessories.

The effluent water used in this work was obtained from the Naval Torpedo Station. It was representative of *Otto Fuel* wastewater that had passed through several columns of activated carbon to remove the explosive PGDN. The wastewater was a mixture of fresh and seawater contaminated with *Otto Fuel*.

Water obtained from the charcoal cleanup process contained enough ionic conductivity to serve as an excellent electrolyte for single-sweep polarography. The pH of this water was 6 to 8. No interference from ions such as Cu^{2+} , Pb^{2+} , and Cd^{2+} were observed with this effluent; thus, the region of voltage where the PGDN gives a polarographic wave (-0.30 to -0.80 V versus Hg pool) is free of interference from the ions that are most commonly found in this region in natural, waste, and seawater. The limit of detection of these ions, with the polarographic technique described in this report, is 20 parts-per-billion and would indicate that the effluent water used in this study was free of Cu^{2+} , Pb^{2+} , and Cd^{2+} to the 20 parts-per-billion level. If metal ions of this type are encountered in a concentration above 20 parts-per-billion in the effluent water, they may be removed from interfering in the analysis of PGDN by the addition of a part-per-million solution of ethylenediaminetetraacetic acid (EDTA).

If the pH and/or ionic content of an effluent water are found to vary considerably, then a buffer near a pH of 7 and of constant ionic strength should be added to the aliquot of effluent water before a polarographic measurement is made. This ensures that the peak potential and total current for PGDN, or other organic material of interest in the voltage range of sweep, do not change with the samples of effluent water being analyzed.

FIELD POLAROGRAPH

A circuit diagram of the field polarograph is shown in Figure 3. A detailed description of the circuitry, operational characteristics, performance, etc. of the polarographic field unit is given in Part 2 of this report.

Originally, the field polarograph was to be designed after the A-1660 Davis *Polarotrace* using digital circuitry. However, it soon became apparent that in order to perpetuate the timing sequence produced by the A-1660 electron tube version an analog unit would have to be built, and the output converted to a digital word. The field unit connects directly to the A-1661A DME stand (Figure 1) and the electrical requirements to operate the stand are designed to be the same as those of the tube model. Adjustments are provided within the field unit to facilitate setting the scaling of these plots. Integrated circuitry is incorporated throughout the design with a minimum of discrete components. The unit is completely self-contained and is very compact. Most of the weight is attributed to the self-contained power supplies. A battery

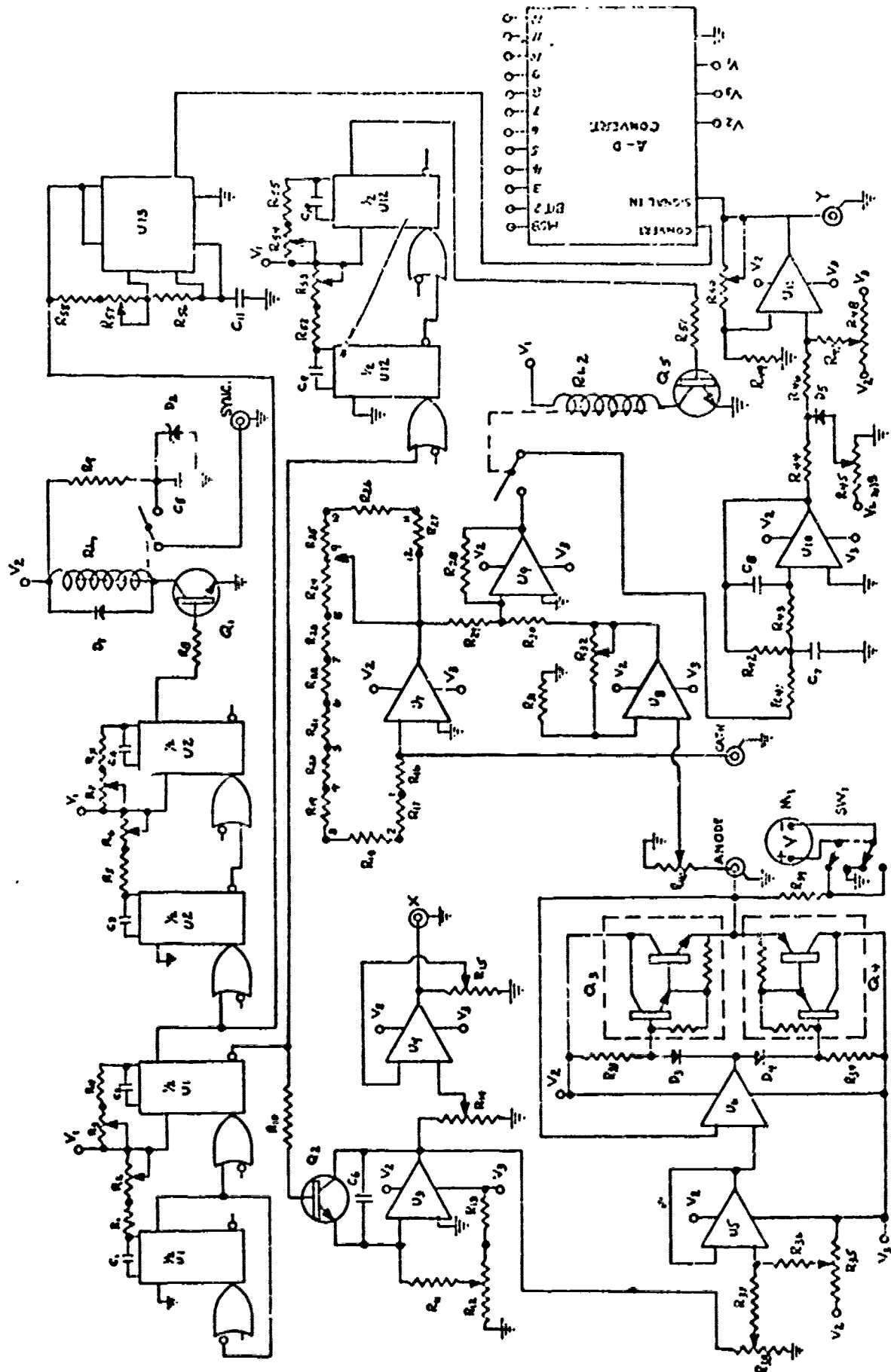


FIGURE 3. Field Polarograph (Circuit Diagram).

pack can be connected externally, making the polarograph truly a field unit.

A block diagram of the field polarograph is shown in Figure 4. A description of the components in each block and discussion of their functional operation in the integrated circuitry of the instrument follows.

Clock. The master clock, running at a metastable state, is designed to control the synchronization and timing of the DME, sweep circuitry, timing of the potential across the cell, sampling selection, and the timing of the analog-to-digital conversion. The circuit consists of a pulse generator with the capability of a variable pulse width and delay.

Sync Control. The time interval controlling the formation of the mercury drop and its removal is the responsibility of the sync control circuit. This stage takes the metastable clock pulses and delays and shapes them, so that the drop of mercury is at a maximum size just prior to and during the sampling. Immediately following the sampling, the drop of mercury is removed from a capillary tube by the actuation of a solenoid. Since the master clock controls this circuit as well as the potential across the cell, sampling is assured of being taken at precisely the correct time.

Sweep Generator. The purpose of the sweep generator is to produce a sweep potential to be applied directly to the cell, and at the same time produce a driving signal for the "x" amplifier. The sweep generator produces a linear ramp directly in concert with that of the clock timing pulses, which assures that the cell readings are taken at the correct time.

X-Amplifier. In order to record and visually see the results of DME polarography, it is necessary to produce a drive signal on the x-ordinate. The signal to the x-amplifier is taken directly from the sweep generator and amplified by the action of a linear amplifier. It is then taken to an external output from which it can be connected to a piece of peripheral equipment. A provision has been incorporated whereby this signal may be varied making it possible to control the length of the linear sweep. This is sometimes desirable when one wishes to expand or reduce the wavefront recording.

Start Potential. This circuit consists of a differential amplifier constructed to algebraically add a DC potential to the sweep signal. This potential is used to determine or identify the unknown substance in solution, and because of this it must be accurately controlled and monitored. In conjunction with this circuit is an analog meter used to monitor the DC potential placed across the cell prior to and during polarographic readings. Start potentials may be either positive or negative and are selected as such by the operator.

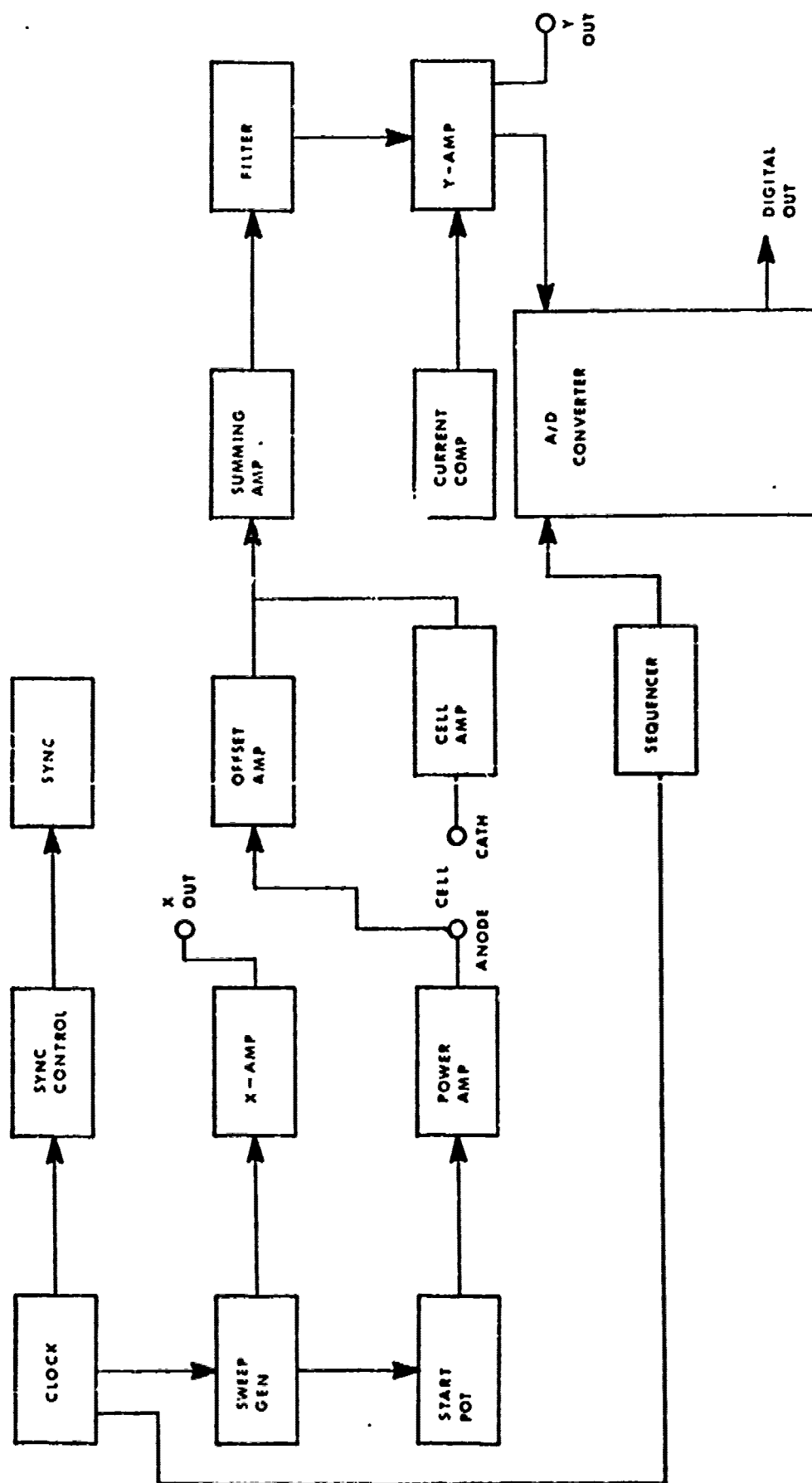


FIGURE 4. Field Polarograph (Block Diagram).

Power Amplifier. Prior to this circuit there has been no amplification of sweep or start potential of sufficient magnitude to drive a signal across the cell without some loss or distortion. In order to prevent this situation, a power amplifier is inserted at this point. The circuit features a low standby current, yet contains a high current drive capability with excellent linearity.

Cell Amplifier. The main purpose of the cell amplifier is to convert the current signals from the cell into a voltage and at the same time amplify these signals up to a point where they can be further processed. Twelve positions of current gain are readily accessible for selection by an external dial. Another desirable attribute of this circuit is that it has an extremely high input impedance - a necessary quality to keep from loading the cell, resulting in erroneous readings. Since cell currents dealt with in this circuit are in many cases in the nanoampere region, care in selection of components associated with this current is essential.

Summing Amplifier. Voltage signals from the cell amplifier contain, in addition to signal information, a slope due to the sweep amplifier. In order to minimize this slope, these signals are summed algebraically with negative slope signals from the offset amplifier.

Low Pass Filter. When detecting very low level signals, the gain of the cell current amplifier is increased. This increase in amplitude also increases unwanted random noise. In order to remove or greatly attenuate this noise and increase the signal-to-noise ratio, an active filter is incorporated. Signals not occurring within the time domain of the sampling period are attenuated to such a degree they cannot be seen at the output.

Current Compensation. Occasionally, there is a signal jump from zero to some positive potential due to an electrical characteristic of the cell and the intense gain of the current amplifier. In order to minimize and compensate for this, a current compensating network is used. This circuit is externally controlled and compensation is made by simply adjusting a potentiometer.

Y-Amplifier. The final ordinate to be displayed on the external equipment is the vertical information, comprised of the analog signals produced and amplified from the cell. Until now the signal information has been of a low level amplitude. It is now necessary to magnify this to such an extent that it may be recorded and displayed as useful information. To accomplish this task a high gain voltage amplifier is employed. Another useful part of this circuit is a y-positioning unit.

Analog-to-Digital Converter. Actually, this part of the field polarograph consists of two circuits: a sequencer and a modular analog-to-digital converter, with a connection to the outside to facilitate in

the external storage of digital information. Information is taken directly from the y-amplifier and fed simultaneously to the analog output as well as the analog-to-digital converter. The sampling rate is determined by a sequencing circuit which is set to run at 10 samples/second. However, there is also a switch that can be actuated so that the converter will run at an external rate compatible with a piece of peripheral equipment. Each analog voltage is converted to a 12-bit digital word at an accuracy of $\pm 1/2$ least significant bit. Polarographic samples can be run with or without this unit. In the laboratory it might find an additional use as a means of viewing the output of the polarograph on a multichannel analyzer, or storage of the digital information on magnetic tape for future reference.

EXPERIMENTAL

POLAROGRAPHIC ANALYSIS FOR PGDN (WITH FIELD POLAROGRAPHS AND A-1660 POLAROTRACE)

Laboratory and Field Samples (Procedure)

A 2-ml or larger aliquot of a natural or effluent water sample is placed in a 5-ml or 15-ml capacity quartz cell to which a small volume of mercury has been added as the anode; the DME, serving as the cathode, is then lowered into the water sample in the cell, which is placed in the constant temperature device and brought to constant temperature. The solution in the cell is now flushed with oxygen-free nitrogen for 3 to 4 minutes to remove all the interfering dissolved oxygen from the water. The start potential of the single-sweep polarograph is set at -0.53 V versus Hg pool and after several sweeps a polarogram is recorded with the X-Y recorder. A typical polarogram for PGDN in effluent water is shown in Figure 5, curve A. A microaliquot of standard PGDN solution is then added to the cell solution and the procedure is repeated. This is known as the standard addition technique and a simple calculation of the PGDN concentration in the sample can be made from a ratio of the two recorded polarogram waveheights. The waveheight for the sample may also be referred to a standard curve of waveheight versus PGDN concentration previously prepared from fresh PGDN solution. The standard curve should be checked frequently if this method is used in the calculation.

In the field a glass cell of the type shown in Figure 1 is placed inside a stainless steel cylinder that controls the temperature of the cell solution to $\pm 0.2^\circ\text{C}$ during the polarographic analysis. The cell was designed for individual or continuous analysis so that the mercury buildup in the cell will be automatically removed when the mercury level reaches the top of the center tube. The cell can be used for about 120 hours of continuous operation before the amount of mercury collected from the DME will reach the level to drain. The cell volume is about 15 ml total capacity and with the DME positioned precisely in the center of the cell there is always enough solution in the cell to cover the DME

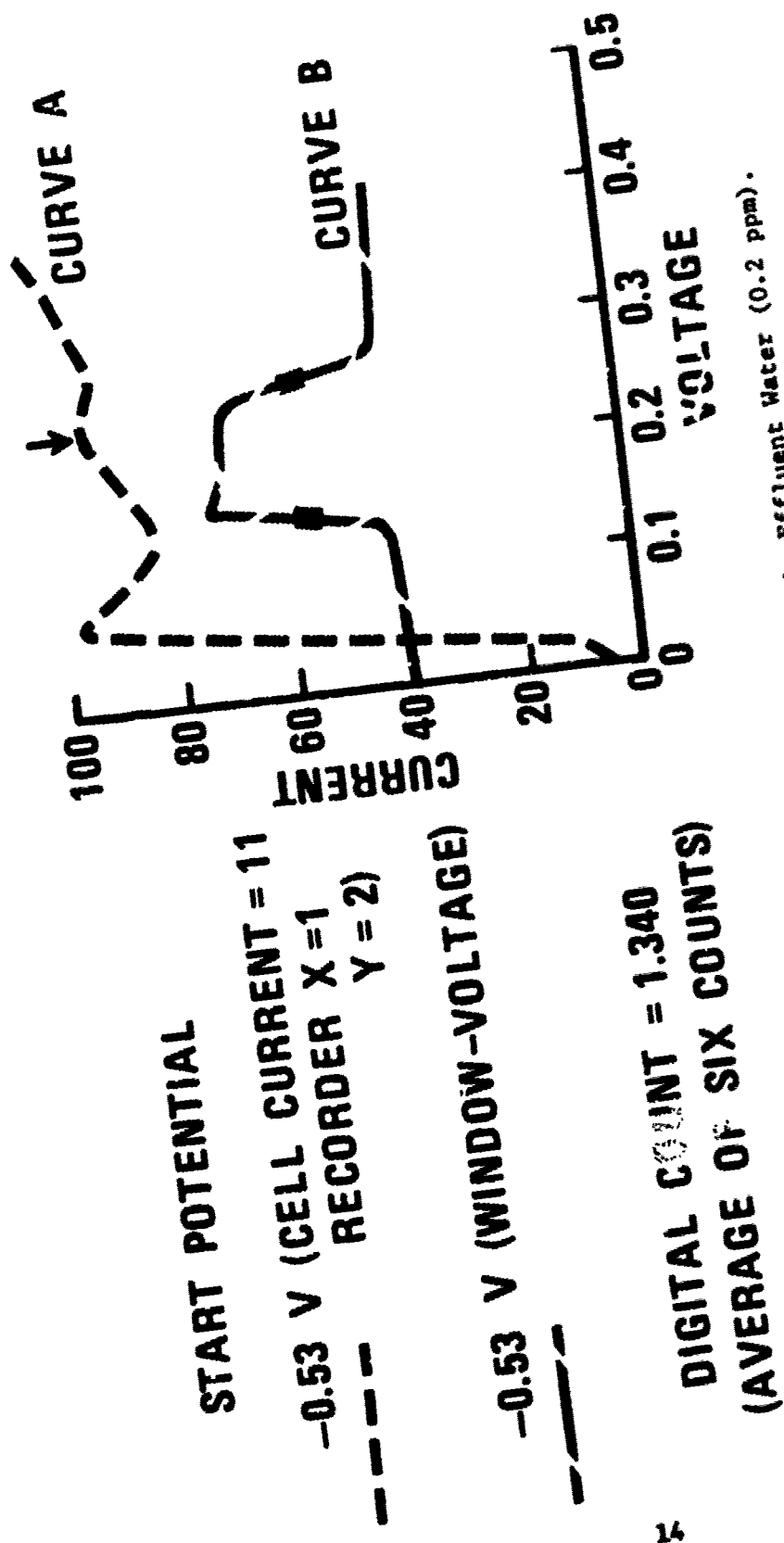


FIGURE 5. Digital Polarographic Analysis of PGIN in Effluent Water (0.2 ppm).

during the analysis. Since the polarograph measures concentration, the cell volume is not critical in the analysis; however, sufficient time must be allowed for complete replacement of the analyzed solution in the cell with new solution before each analysis is made.

Digital Polarograph and Monitoring System

If the digital polarograph (Figure 3) is used for the analysis, a digital count is recorded in the easy view window of the instrument every 28 seconds after the analytical procedure above has been followed through the nitrogen flush stage and the instrument has been turned on with the start potential again set at -0.75 V. The window setting for the digital polarograph recording is shown in Figure 5, curve B. Thus, it can be seen that the instrument records a number for the largest current in the voltage range where the complete polarogram for PGDN is seen. The peak potential for PGDN occurs at -0.75 V. This is well within the window setting for the analysis of a low concentration of PGDN such as present in the effluent water from the carbon absorption process. A digital count change of about 100 with the polarograph represents about 20 parts-per-billion change in PGDN concentration in the effluent water. A preselected number, representing a critical concentration of PGDN, is set into the concentration select window on the polarograph and an alarm built into the instrument will be set off if the concentration (digital number) exceeds this number by one digit. For example, if a concentration of 100 parts-per-billion is unacceptable in the effluent water, then a number of 750 (representing that concentration and previously determined in standard addition experiments) is dialed in. The alarm will not sound as long as the concentration of PGDN in the effluent water remains less than 100 parts-per-billion, but it will sound as soon as the dialed-in number (750) is exceeded by one digit (751) in the digital number showing in the easy view window of the polarograph. The digital number repeats every 28 seconds and a plant operator can push a reset button at any time to obtain a new reading to verify the concentration of PGDN in the effluent stream. This process can be repeated as many times as necessary to confirm water purity in PGDN.

RESULTS AND DISCUSSION

The polarographic analytical procedures, field polarographs, and complete monitoring system developed in this laboratory have been used successfully at Naval Weapons Center (NWC) to determine and monitor PGDN in effluent water of the type discussed in this report. The lower limit of detection is 20 parts-per-billion and concentrations as low as 50 parts-per-billion of the explosive can be monitored and determined within ± 5 to 10% of the true amount present in the water. An individual analysis for PGDN can be performed on a 2-ml aliquot of effluent water within 5 minutes and during continuous operation a concentration reading

NWC TP 5860, Part 1

can be obtained every 28 seconds with the digital polarograph and every 7 seconds with the analog polarograph.

Data obtained for PGDN concentration in typical effluent water from a carbon adsorption process, with the digital polarograph and monitoring system described in this report, are shown in Table 1. The data compare favorably with data obtained by both the thin-layer and vapor-phase chromatographic methods.^{2,3} A range from 0.10 to 1000 ppm PGDN could be measured satisfactorily with the polarographic monitoring system. Samples containing over 150 ppm PGDN needed to be diluted before analysis. Either KCl or NaCl (0.1 M) solution could be conveniently used for this dilution. Well defined polarograms were observed in all cases for analytical purposes.

TABLE 1. Polarographic Analysis of Effluent and Wastewater for PGDN (Data Obtained with Field Polarograph).

Sample	pH	PGDN, ppm
Effluent No. 1	7.50	0.12
Effluent No. 2	8.05	0.37
Effluent No. 3	6.35	0.35
Column No. 1	6.90	2.06
Column No. 2	7.10	1.91
Column No. 1A	8.40	1.54
Feed, pretreated	6.50	167.00
Feed, original wastewater	6.20	1062.00

Table 2 shows typical analog and digital data obtained on the same sample of effluent water with the digital field polarograph operating with the auxiliary monitoring equipment. A digital count change of 100 represents a PGDN concentration change in the effluent water of 20 parts-per-billion. The X-Y recorder showed only a 1.0 division change on graph paper (10 X 10 to 1/2 inch) for this change in PGDN concentration. Thus, the digitally recorded data reflect more sensitivity to a slight change in PGDN concentration in the effluent water obtained from the carbon cleanup columns.

Standard additions of a pure PGDN solution to 2-ml aliquots of the effluent water showed that this explosive gives well defined polarograms directly in this media, with waveheights that are proportional to concentration over the range of 10^{-6} to 10^{-9} g/ml. A polarogram of this type can be recorded every 7 seconds with the field polarographs. The digital version records an average current taken from four successive 7-second mercury drops from the DME, and a digital count, representing

the total current reached at the peak potential within the voltage window setting of the instrument, is seen in the easy view window of the polarograph every 28 seconds. The current-voltage relationship can also be monitored with an oscilloscope.

TABLE 2. PGDN in Effluent Water (Analog and Digital Polarographic Data).

X-Y Recorder ^a	Digital count ^b	PGDN conc ^c , ppm
8.0	1.205	0.19
9.0	1.312	0.21
10.0	1.407	0.24
12.0	1.628	0.29

^a Graph paper divisions 10 X 10 to 1/2 inch.

^b Average of six counts (cell current = 11).

^c Determined by standard addition technique.

A two-electrode system of DME versus Hg pool was used in most of this analytical work where small currents are being measured, as the potential of the Hg pool (reference electrode) remained relatively constant over the entire small applied potential range used for the analysis of PGDN in the type of effluent water obtained from the carbon adsorption process. A three-electrode system should be used if potential changes might occur in the reference electrode during the analysis. Most commercially available polarographs make use of the three-electrode system, where the potential applied to the polarographic cell is automatically controlled on a continuous basis to compensate for the effects of electrolyte resistance. The resistance of the carbon adsorption effluent water (electrolyte) was found to be relatively constant and did not seriously affect the analytical results when a two-electrode system was used. A saturated calomel electrode could conveniently be used as the reference electrode with a DME and Hg pool in a three-electrode system, for the analysis on a continuous basis in the field where uncertainties and/or changes in the quality of the effluent water could affect the analytical data.

State-of-the-art methods sometimes make it possible to eliminate concentrating a sample. This appears to be true in the case of the carbon adsorption column effluent when the concentration of the explosive pollutant is still large enough to determine it directly in the media without interference from other contaminants that have been removed by the carbon.

CONCLUSIONS AND RECOMMENDATIONS

A simple, rapid, and unique single-sweep polarographic analysis with new field instrumentation for specifically monitoring the explosive PGDN in effluent water has been developed in this laboratory. The analytical technique and equipment are described in this report and are applicable to both laboratory and field use for the analysis of many other organic and inorganic pollutants in natural and effluent water. It is suggested that the polarographic procedure and instrumentation developed for the analysis of PGDN be extended to other amenable compounds of Navy interest such as HMX, RDX, TNT and derivatives, nitroguanidine and tetranitromethane.

A series of tests designed to show the reliability of the analytical procedure and complete monitoring system under operating conditions at test sites is needed. These tests should show if the present monitoring system concept is well suited to *in situ* measurement.

Since no Environmental Protection Agency- or American Society for Testing and Materials-approved methods of analysis exist for explosives and many other organic pollutants found in water in the environment, the polarographic procedures described in this report should be investigated by the Navy as potentially approved methods, particularly with regard to legal environmental problems the Navy may have with ordnance-related facilities.